

Theoretical study of deuterated PAHs as carriers for IR emission features in the ISM

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ABSTRACT

This work proposes deuterated PAH (DPAH⁺) molecules as a potential carrier of the 4.4 and 4.65 μm mid infrared emission bands that have been observationally detected towards the Orion and M17 regions. Density Functional Theory calculations have been carried out on DPAH⁺ molecules to see the variations in the spectral behaviour from that of a pure PAH. DPAH⁺ molecules show features that arise due to the stretching of the aliphatic C-D bond. Deuterated PAHs have been previously reported as carriers for such features. However, preferred conditions of ionization of PAHs in the interstellar medium (ISM) indicates the possibility of the formation of DPAH⁺ molecules. Comparison of band positions of DPAH⁺s shows reasonable agreement with the observations. We report the effect of size of the DPAH⁺ molecules on band positions and intensities. This study also reports a D/H ratio ($[\text{D}/\text{H}]_{\text{sc}}$; the ratio of C – D stretch and C – H stretch bands per $[\text{D}/\text{H}]_{\text{num}}$) that is decreasing with the increasing size of DPAH⁺s. It is noted that large DPAH⁺ molecules (no. of C atoms ~ 50) match the D/H ratio that has been estimated from observations. This ratio offers prospects to study the deuterium abundance and depletion in the ISM.

Key words: molecular processes – ISM: lines and bands – ISM: molecules – molecular data

1 INTRODUCTION

In recent years, the detection of unidentified infrared (UIR) emission bands at 3.3, 6.2, 7.7, 8.6, 11.2, 12.7 and 16.4 μm towards many astronomical objects in the interstellar medium (ISM) has opened up new prospects in observational, laboratory and theoretical molecular astrophysics. These bands were first detected by Gillett et al. (1973) as broad emission features together with line as well as continuum radiation towards three planetary nebulae NGC 7027, BD+30°3639 and NGC 6572. *ISO* (SWS) and *Spitzer* observations have revealed that these features are ubiquitous in the ISM (Cox & Kessler 1999; Smith et al. 2007). With the progress in observational astronomy, these features have further been observed towards a variety of astronomical objects including H II regions, reflection nebulae, planetary nebulae, photodissociation regions, AGB objects, active star forming regions, young stellar objects, diffuse medium, etc. (Onaka et al. 1996; Mattila et al. 1996; Verstraete et al. 1996; Moutou et al. 1999; Hony et al. 2001; Verstraete et al. 2001; Peeters et al. 2002; Abergel et al. 2002; Acke & van den Ancker 2004; Sakon et al. 2004). These features are also observed in external galaxies of varying metallicity (Genzel et al. 1998; Mattila et al. 1999; Helou et al. 2000; Lu et al. 2003; Regan et al. 2004; Brandl et al. 2006; Armus et al. 2007; Onaka et al. 2008; Mori et al. 2012). Apart from strong UIR band emission, there are weak broad features distributed in the emission plateaux in the $\sim 3 - 20 \mu\text{m}$

range (Tielens 2008). Depending on the physical conditions of the observed environment, source to source variation of the observed IR features is noticed in terms of peak position, width and intensity, however, an overall correlation among the bands is maintained (Hony et al. 2001; Peeters et al. 2002; Sakon et al. 2007; Tielens 2008; Mori et al. 2012).

It was first proposed by Léger & Puget (1984) and by Allamandola et al. (1985) that these features arise due to excitation of polycyclic aromatic hydrocarbon (PAH) molecules. When a PAH molecule absorbs an UV photon, it is either ionized or it gets excited to a higher electronic state. These excited PAHs tend to relax through radiation-less processes, including dissociation, internal conversion and intersystem crossing. As a consequence, the molecule comes to its ground electronic state while still in a vibrationally excited state. The molecule emits through IR emission which reverts it back to its ground state. The excess energy is released off through different modes of vibration, giving rise to IR emission features (Allamandola et al. 1989; Puget & Léger 1989). Though the widespread presence of PAHs has been established by the observation of UIR bands, the assignment of the exact PAH form responsible for these bands still presents some challenges. Several weaker bands have been detected by Short Wavelength Spectrometer (SWS) on board the *ISO* satellite (Verstraete et al. 1996; Peeters et al. 2004). In order to assign carriers for these

bands, it is essential to compare the observational data with experimental as well as theoretical spectral data.

PAHs constitute a significant fraction of the material in the ISM bearing about 5-10% of the elemental carbon (Tielens 2008) and contribute in various interstellar processes like heating of the ISM through the photoelectric effect and influence on the charge balance inside molecular clouds (d'Hendecourt & Léger 1987; Lepp & Dalgarno 1988; Verstraete et al. 1990; Bakes & Tielens 1994; Peeters et al. 2004). It is important to study the formation of PAHs in astrophysical environments in order to understand the chemical processes occurring in the ISM. PAHs have also been proposed to be the carriers of the Diffuse Interstellar Bands (DIBs) observed towards Galactic and extragalactic sources (Crawford et al. 1985; Léger & d'Hendecourt 1985; Salama et al. 1996, 2011; Cox et al. 2006). Interstellar PAHs encompass a vast range of families and a single category of PAH alone cannot explain the complete set of UIR bands. Several substituted PAHs have been studied theoretically and experimentally in order to seek to match the UIR bands. These include nitrogen substituted PAHs (Cook et al. 1996; Bauschlicher 1998a; Mattioda et al. 2003, 2005; Hudgins & Allamandola 2004; Hudgins et al. 2005; Alvaro Galué et al. 2010), oxygen substituted PAHs (Cook et al. 1996; Bauschlicher 1998b; Hudgins et al. 2005), silicon substituted PAHs (Hudgins et al. 2005), methyl substituted PAHs (Bauschlicher & Langhoff 1998), and PAHs with Fe and Mg (Serra et al. 1992; Klotz et al. 1995; Hudgins et al. 2005; Simon et al. 2011).

Among the substituted PAHs, deuterated PAHs (PADs) have been studied extensively both experimentally and theoretically in relation to the UIR bands (Bauschlicher et al. 1997; Hudgins et al. 2004). PADs show distinct features at 4.4 and 4.65 μm that have been observed towards Orion Nebula and M17 (Peeters et al. 2004). These observations have not been confirmed by *AKARI* observations (Onaka et al. 2014). These emission bands are characteristics of C – D stretching modes in PADs (Peeters et al. 2004). Deuterium (D) detection in the ISM established by the higher Lyman lines seen in *FUSE* spectra (Hoopes et al. 2003) further justifies the existence of PADs in the ISM. Interstellar PAHs may become deuterium enriched by exchange of D from D_2O ice when exposed to UV radiation (Sandford et al. 2000a). The 4.4 and 4.65 μm bands provide a good prospect for observational searches for PADs as they do not overlap with any other PAH features and are a pure C – D contribution (Hudgins et al. 2004). Interstellar PADs are proposed to be a major reservoir for D which may explain the present D/H ratio in the ISM (Draine 2006). Linsky et al. (2006) discussed a variation in D/H ratios along various lines of sight in the Milky Way and beyond. According to the ‘Deuterium depletion model’, Draine (2006) proposed a D/H ratio of ~ 0.3 in PAHs. A similar ratio is obtained by Peeters et al. (2004). However, *AKARI* data did not confirm this and does not support the presence of large amount of PADs in the ISM (Onaka et al. 2014).

In this work we consider another class of deuterium enriched PAHs, deuterated PAHs (DPAH^+)¹. DPAH^+ molecules might be crucial in an astrophysical context because their closed-shell electronic structure makes them stable enough to survive the extreme interstellar environment. Here, we report theoretical vibrational calculations of DPAH^+ as probable carriers of some UIR bands and make comparison with observed UIR features.

¹ deuterated PAHs are PAHs to which a deuteron is added - the equivalent of protonated PAHs for a proton.

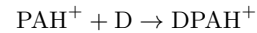
2 PROBABLE DPAH^+ FORMATION MECHANISM IN THE ISM

Deuterium is considered to be one of the lightest elements formed after the Big Bang and in the chemical evolution of the Universe, it is converted to heavier elements by nuclear fusion in stellar interiors. The present lower value of D/H ($\sim 7\text{ppm}$ to $\sim 22\text{ppm}$); (Jenkins et al. 1999; Sonneborn et al. 2000; Wood et al. 2004) compared to the primordial one ($\sim 26\text{ppm}$) (Epstein et al. 1976; Mazzitelli & Moretti 1980; Moos et al. 2002; Steigman 2003; Wood et al. 2004) is explained by this. However, Draine (2006) argued that it is highly possible that some primordial deuterium is depleted in interstellar dust. Draine (2006) further suggested that of all the interstellar dust grains incorporating deuterium, some may be in PAHs that may result in the formation of PADs. Deuterated PAHs (PADs or $\text{D}_n\text{-PAHs}$) may be formed in the ISM by the following chemical processes

i) gas-phase ion-molecule reactions in low temperature environments (Tielens 1997), ii) gas-grain reactions (Tielens 1983, 1992, 1997), iii) photodissociation of carbonaceous dust grains (Allamandola et al. 1987, 1989) and iv) exchange of deuterium in D_2O ice with one of the peripheral hydrogen atoms of an interstellar PAH when exposed to UV radiation (Sandford et al. 2000b).

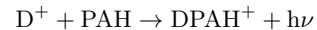
Formation of DPAH^+ molecules may result from a number of interstellar processes. These include:

(i) Addition of D to PAH radical cations:

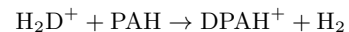
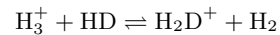


Le Page et al. (1997), Snow et al. (1998), and Le Page et al. (2001) discussed the reaction of PAH cations with atomic and molecular hydrogen to form protonated PAHs (HPAH^+) that might emerge as a potential carriers of DIBs (Pathak & Sarre 2008). Larger PAH cations tend to associate efficiently with atomic H to form HPAH^+ in interstellar environments (Herbst & Le Page 1999). In a similar way, deuterium atoms may also react with PAH cations to form deuterated PAHs.

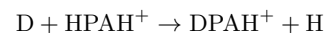
(ii) Addition of D^+ , produced by direct ionization and charge-transfer reaction, to a neutral PAH to form DPAH^+ :



(iii) Low temperature ion-molecule reaction followed by deuterium fractionation: At temperatures below 50 K, deuterium fractionation is significant (Millar et al. 1989). Interstellar deuterium mostly exists in the form of HD. Fractionation of HD by exchange reaction with H_3^+ occurs efficiently in low temperature dense interstellar clouds, to form deuterated molecular ions H_2D^+ (Millar et al. 1989). H_2D^+ has a low deuteron affinity (Roberts et al. 2002) and can transfer D^+ to PAH to form DPAH^+ .



(iv) D may merely replace the hydrogen at the protonation site in HPAH^+ without altering the network to form DPAH^+



Due to the higher mass of deuterium in DPAH^+ , such interstellar species are expected to give spectral modes (associated with D) towards longer wavelengths compared to their neutral or protonated counterparts.

3 COMPUTATIONAL APPROACH

Theoretical quantum chemical calculations help in narrowing down candidates for much more expensive laboratory experiments. Considering the high cost, time consumption and other constraints faced in laboratory, theoretical computational study can propose selected PAHs for which laboratory spectroscopy can most usefully be performed. Density Functional Theory (DFT) has been used rigorously to calculate the harmonic frequencies and intensities of vibrational modes of PAHs in various forms including size, composition and charge states (Langhoff 1996; Bauschlicher et al. 1997; Bauschlicher & Langhoff 1997; Langhoff et al. 1998; Hudgins et al. 2001, 2004; Pathak & Rastogi 2005, 2006, 2007; Pathak & Sarre 2008; Candian et al. 2014). In the present work, DFT in combination with a B3LYP functional and a 6-311G** basis set has been used to optimize the molecular structures of PAHs. The optimized geometry is used to obtain the vibrational frequencies of various modes at the same level of theory. Theoretical calculations tend to overestimate the frequency compared to experiments (Langhoff 1996). The use of a larger basis set, *e.g.* 6-311G**, generally reduces the overestimation compared to smaller basis sets (Langhoff 1996). Use of a larger basis set compared to a smaller one also shows good agreement with experiment. However, the use of a large basis set does not support use of a single scaling factor for all of the vibrational modes (Langhoff 1996). In order to evaluate the mode-dependent scaling factors, calibration calculations were made for selected PAHs, both neutral and ionized. On comparing the theoretical frequencies with matrix isolated spectroscopic experimental data (Hudgins & Allamandola 1995a,b; Hudgins & Sandford 1998a,b), three different scaling factors have been determined. The scaling factors obtained are 0.974 for the C – H out-of-plane (oop) mode, 0.972 for the C – H in-plane and C – C stretching modes and 0.965 for the C – H stretching mode. Gaussian line shapes of 30 cm⁻¹ FWHM are used to plot the computationally obtained spectra. Our sample includes deuterated pyrene (DC₁₆H₁₀⁺), deuterated perylene (DC₂₀H₁₂⁺) and deuterated coronene (DC₂₄H₁₂⁺). Isomers of DC₁₆H₁₀⁺ and DC₂₀H₁₂⁺ have also been included. The data presented here were produced using GAMESS quantum chemistry suite of programs (Schmidt et al. 1993).

4 RESULTS AND DISCUSSION

Deuterated pyrene

Fig. 1 shows the theoretical spectra of deuterated pyrene (DC₁₆H₁₀⁺) and its isomers. Each isomer shows a unique spectrum. Deuterated pyrene with C_{2v} symmetry (Fig. 1a) shows pronounced transitions particularly in the 825–1600 cm⁻¹ (12.12–6.25 μm) range compared to its isomers with C_s symmetry (Fig. 1b and Fig. 1c). Most of the bands are characteristic of C – H out-of-plane (oop), C – H in-plane, C – C stretching and C – H stretching modes. However, some new features arise due to the contribution of D. These include C – D in-plane, H – C – D oop and C – D stretching particularly. The C – D in-plane modes are distributed in the ~ 700 – 870 cm⁻¹ (14–11 μm) range with varying relative intensities between 0.05 to 0.4. This is the same region where C – H oop occurs in unsubstituted PAHs. The H – C – D oop modes are relatively strong and present in the narrow range of 1125–1185 cm⁻¹ (8.4–8.9 μm). The C – D in-plane and H – C – D oop modes are found to be blended with other fundamental modes. A significant aliphatic C – D stretching mode ap-

pears at 2092 cm⁻¹ (4.78 μm) in Fig. 1a and faintly in the other two isomers at 2116 cm⁻¹ (4.73 μm) and 2103 cm⁻¹ (4.76 μm) (Fig. 1b and Fig. 1c). Absolute intensities for the C – D stretching modes are 18.128 km/mole, 8.132 km/mole and 11.682 km/mole respectively for the three isomers.

The C – D stretching mode at 4.78 μm does not overlap with any other mode and appears as a new feature. There is also an aliphatic C – H bond in deuterated pyrene at the addition site of deuterium. A spectral band near ~ 2850 cm⁻¹ (3.5 μm) is attributed to aliphatic C – H stretching, while those near ~ 3060 cm⁻¹ (3.3 μm) are due to aromatic C – H stretching. D-associated modes for deuterated pyrene and its isomers are presented in Table 1. Relative intensities above 0.05 only are listed.

DFT calculations have been carried out on neutral pyrene, cationic pyrene, deuterated pyrene and protonated pyrene to compare the spectra with deuterated pyrene. Fig. 2 shows comparison of these spectra with that of deuterated pyrene. Deuterated pyrene is transitionally active in the ~ 900 – 1600 cm⁻¹ (11–6 μm) range (Fig. 2e). This is reasonably similar to protonated pyrene with a variation in intensity (Fig. 2d). For deuterated pyrene, the intensities of the C – H in plane and C – C stretching modes are increased by a factor of ~ 1.2 compared to protonated pyrene. Deuterated pyrene being structurally similar to protonated pyrene shares similar types of vibrational characteristic modes. However, due to the larger mass of deuterium, all D-associated modes in deuterated pyrene are red-shifted compared to the protonated form; the H – C – D oop mode shifts from 1278 cm⁻¹ (7.82 μm) to 1126 cm⁻¹ (8.87 μm) compared to its protonated counterpart. This particular mode at 8.87 μm is distinct (Fig. 2e) and does not appear in any other form of pyrene. Another striking difference is the presence of a mode at 2092 cm⁻¹ (4.78 μm) (Fig. 2e) in deuterated pyrene which is assigned to C – D stretching. On comparing with its protonated counterpart, it seems that the relative intensity (0.3) of the H – C – H symmetric stretching mode at 2854 cm⁻¹ (3.5 μm) in protonated pyrene is divided between the C – D stretching mode (relative intensity 0.14) at 2092 cm⁻¹ (4.78 μm) and the aliphatic C – H stretching mode (relative intensity 0.21) at 2853 cm⁻¹ (3.5 μm) for deuterated pyrene. Cationic pyrene also shows significant transitions in the 900–1600 cm⁻¹ (11–6 μm) region (Fig. 2b), but there are fewer modes compared to protonated and deuterated pyrene. This may be due to reduction in the symmetry for deuterated pyrene. Neutral pyrene and deuterated pyrene show weak features in this region and the C – H stretching mode at 3050 cm⁻¹ (3.3 μm) dominates with high intensity (Fig. 2a and Fig. 2c). For cationic, protonated and deuterated pyrene, there are weak bands in the 3.3 μm region. As for deuterated pyrene, the C – D stretching mode also exists for deuterated pyrene (Fig. 2c), but is shifted to shorter wavelength and appears at 2254 cm⁻¹ (4.44 μm).

Deuterated perylene

Deuterated perylene (DC₂₀H₁₂⁺) has three isomers and the spectra are presented in Fig. 3. All the isomers have C_s symmetry and contain D-contributing features along with the other usual PAH bands. C – D in-plane features are present between 730 – 870 cm⁻¹ (13.7–11.5 μm) and H – C – D oop in the 1120 – 1212 cm⁻¹ (8.9–8.3 μm) range. The C – D stretching mode appears at 2087 cm⁻¹ (4.79 μm) (Fig. 3a) and is not distinct in the other two isomers (Fig. 3b & Fig. 3c). Absolute intensities for the C – D stretching mode for the three isomers of deuterated pery-

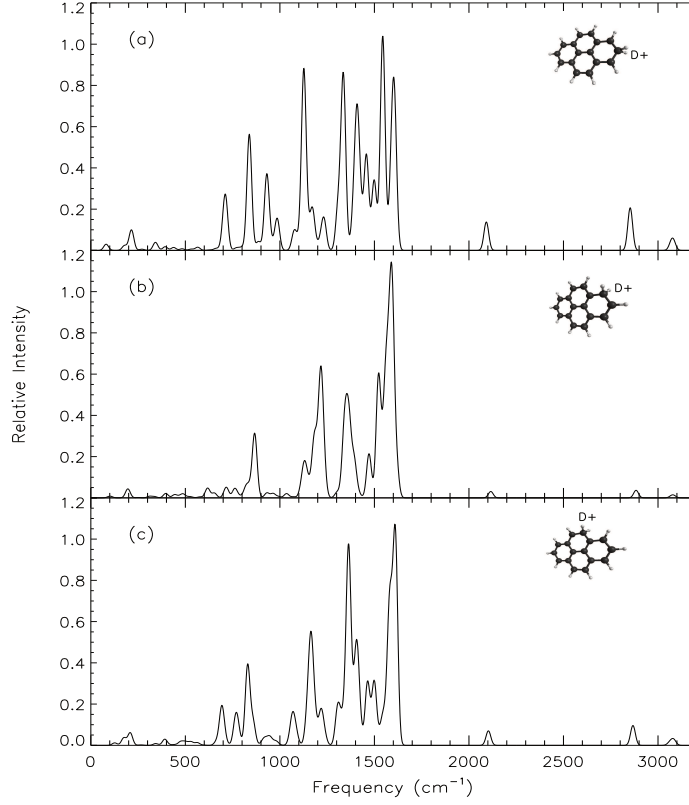


Figure 1. Theoretical spectra of (a) $\text{DC}_{16}\text{H}_{10}^+$, (b) Isomer 1 of $\text{DC}_{16}\text{H}_{10}^+$, (c) Isomer 2 of $\text{DC}_{16}\text{H}_{10}^+$

Table 1. Theoretical spectral data for Deuterated pyrene and its isomers

DPAH^+	Frequency (cm^{-1})	Wavelength (μm)	Relative Intensity	Mode
Deuterated Pyrene	700	14.29	0.05	C – D in plane + C – C – C in plane
	1126	8.87	0.86	H – C – D oop + C – H in plane
	2092	4.78	0.14	C – D stretching
Deuterated Pyrene (isomer1)	866	11.54	0.31	H – C – D in plane + C – H oop
	1176	8.5	0.1	H – C – D oop + C – H in plane
	1185	8.44	0.19	H – C – D oop + C – H in plane
Deuterated Pyrene (isomer2)	764	13.08	0.08	C – D in plane + C – C – C in plane + C – H oop
	829	12.06	0.39	C – D in plane + C – H oop
	858	11.65	0.11	C – D in plane + C – H oop
	1163	8.6	0.4	H – C – D oop + C – H in plane
	1171	8.54	0.1	H – C – D oop + C – H in plane
	2103	4.76	0.07	C – D stretching

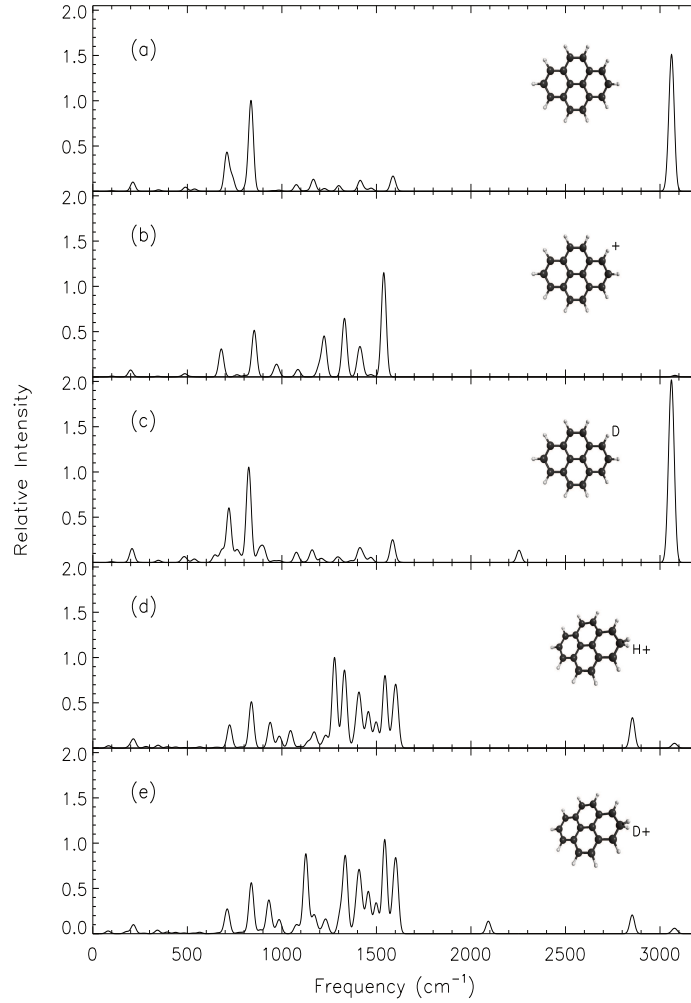


Figure 2. Theoretical spectra of (a) Neutral pyrene, (b) Pyrene cation, (c) Deuterated pyrene, (d) Protonated pyrene and (e) Deuterated Pyrene

lene are 14.073 km/mole, 5.004 km/mole and 4.582 km/mole respectively. Bands near $\sim 2850 \text{ cm}^{-1}$ ($3.5 \mu\text{m}$) and $\sim 3060 \text{ cm}^{-1}$ ($3.3 \mu\text{m}$) account for aliphatic C – H stretching and aromatic C – H stretching of deuterated perylene, respectively. Spectral data for D-contributing modes with relative intensities above 0.05 are presented in Table 2.

A comparison of the theoretical spectrum of deuterated perylene with its neutral, cation, deuterated and protonated forms is shown in Fig. 4. Deuterated and protonated perylene participate in similar types of vibrational modes with increasing number of transitions in the $900 - 1600 \text{ cm}^{-1}$ ($11\text{-}6 \mu\text{m}$) range compared to their neutral counterparts (peryene and deuterated perylene). Despite the fact that most of the modes are similar in this region, they do vary in intensity. However, variation in intensity is not uniform. Protonated and deuterated perylene show maximum intensity for C – C stretch vibration close to 1550 cm^{-1} ($6.45 \mu\text{m}$) (Fig. 4d & Fig. 4e). For deuterated perylene, H – C – D oop occurs at 1120 cm^{-1} ($8.93 \mu\text{m}$) and 1130 cm^{-1} ($8.85 \mu\text{m}$) mixing with the C – H in plane modes (Fig. 4e). Other forms of perylene

do not show any significant intensity modes near this wavenumber. Deuterated and deuterated perylene show new features at 2291 cm^{-1} ($4.36 \mu\text{m}$) and 2087 cm^{-1} ($4.79 \mu\text{m}$), respectively (Fig. 4c & Fig. 4e). These two transitions arise due to aromatic (deuterated perylene) and aliphatic (deuterated perylene) C – D stretching respectively. All forms of perylene show bands near 3050 cm^{-1} ($3.3 \mu\text{m}$) with varying intensities which is attributed to aromatic C – H stretching. Neutral forms of perylene (peryene and deuterated perylene) show strong intensities at this wavenumber, while cationic, protonated and deuterated perylene have weak features in this region. The presence of an aliphatic C – H bond in protonated and deuterated perylene produces features at 2848 cm^{-1} ($3.5 \mu\text{m}$) and 2846 cm^{-1} ($3.5 \mu\text{m}$) due to stretching of the C – H bond. It is recognized that the intensity of aliphatic H – C – H stretching mode (0.15) in protonated perylene is distributed among intensities of aliphatic C – D stretching (0.06) and aliphatic C – H stretching (0.09) in deuterated perylene.

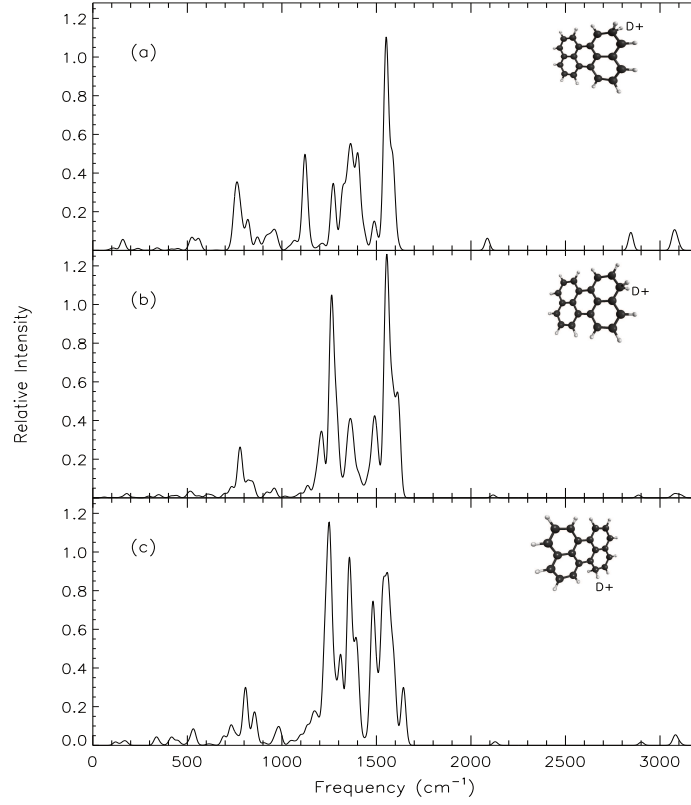


Figure 3. Theoretical spectra of (a) $\text{DC}_{20}\text{H}_{12}^+$, (b) Isomer 1 of $\text{DC}_{20}\text{H}_{12}^+$, (c) Isomer 2 of $\text{DC}_{20}\text{H}_{12}^+$

Table 2. Theoretical spectral data for Deuterated perylene and its isomers

DPAH^+	Frequency (cm^{-1})	Wavelength (μm)	Relative Intensity	Mode
Deuterated Perylene	755	13.25	0.18	C – D in plane + C – H oop
	770	12.98	0.18	H – C – D in plane + C – H oop
	786	12.73	0.06	H – C – D in plane + C – H oop
	870	11.49	0.07	H – C – D in plane + C – H oop
	1120	8.93	0.39	H – C – D oop + C – H in plane
	1130	8.85	0.12	H – C – D oop + C – H in plane
	2087	4.79	0.06	C – D stretching
Deuterated Perylene (isomer 1)	778	12.86	0.23	C – D in plane + C – H oop
	846	11.82	0.07	C – D in plane + C – H oop + C – C – C in plane
	1197	8.35	0.1	H – C – D oop + C – H in plane
	1212	8.25	0.22	H – C – D oop + C – H in plane
Deuterated Perylene (isomer 2)	730	13.7	0.1	C – D in plane + C – H oop
	853	11.73	0.13	C – D in plane + C – H oop + C – C – C in plane
	862	11.59	0.05	C – D in plane + C – H oop + C – C – C in plane

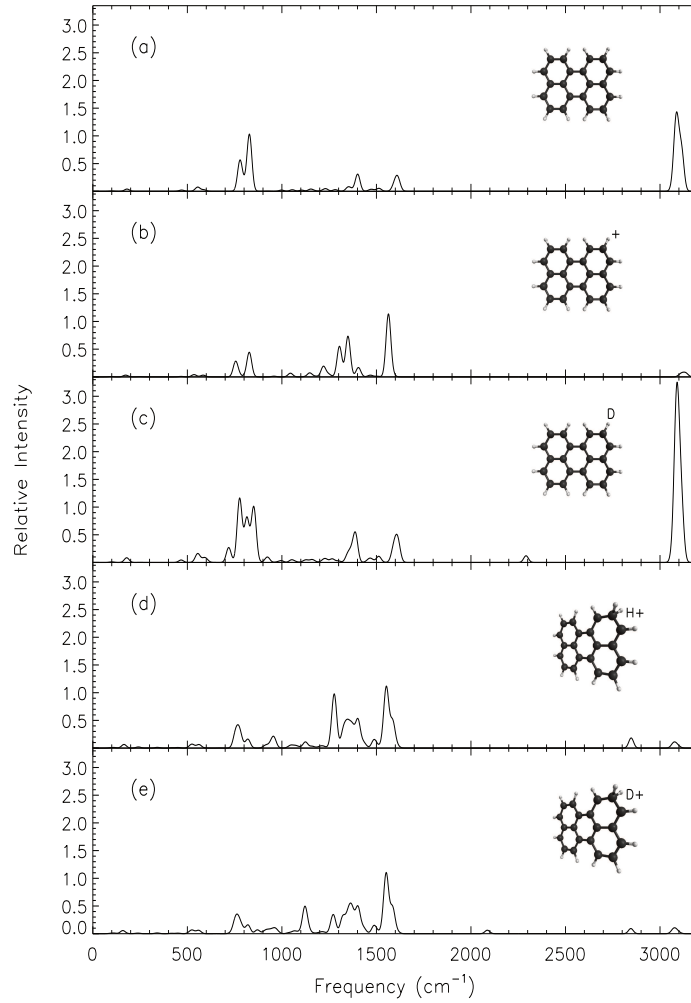


Figure 4. Theoretical spectra of (a) Neutral perylene, (b) Perylene cation, (c) Deuterated perylene, (d) Protonated perylene and (e) Deuterated Perylene

Deuterated coronene

Coronene has only one unique site of deuteration. Fig. 5e shows the theoretically predicted spectrum for deuterated coronene. The C – D in-plane modes are distributed in the $823 - 871 \text{ cm}^{-1}$ ($12.15 - 11.5 \text{ }\mu\text{m}$) region, the H – C – D oop mode is present at 1181 cm^{-1} ($8.47 \text{ }\mu\text{m}$) and the C – D stretching mode appears weakly at 2110 cm^{-1} ($4.74 \text{ }\mu\text{m}$). Absolute and relative intensities for the C – D stretching mode are 7.328 km/mole and 0.04 respectively. The spectral data are listed in Table 3.

Fig. 5 also shows the comparison of deuterated coronene with its neutral, cation, deuterated and protonated forms. For deuterated and protonated coronene, spectral modes in $\sim 1352 - 1612 \text{ cm}^{-1}$ ($7.4 - 6.2 \text{ }\mu\text{m}$) region follow a similar pattern with variation in intensity. Intensities for deuterated coronene are increased by an average factor of ~ 1.4 compared to its protonated form in this region. The maximum intensity for both appears nearly at same position at 1330 cm^{-1} ($7.52 \text{ }\mu\text{m}$), but the corresponding modes are different. For deuterated coronene, the peak intensity arises due to the combination of C – H in-plane and

C – C stretch modes, whereas, for protonated coronene, it is due to the combination of H – C – H oop and C – C stretch modes. The H – C – D oop mode is prominent at 1181 cm^{-1} ($8.47 \text{ }\mu\text{m}$) for deuterated coronene (Fig. 5e). The C – D stretching vibrational mode for deuterated and deuterated coronene fall in a featureless region at 2254 cm^{-1} ($4.44 \text{ }\mu\text{m}$) and 2110 cm^{-1} ($4.74 \text{ }\mu\text{m}$) respectively (Fig. 5c & Fig. 5e). These two modes are weak in intensity. Cationic coronene (Fig. 5b) shows a greater number of transitions in the C – H in plane and C – C stretching region ($900 - 1600 \text{ cm}^{-1}$) compared to its neutral forms (coronene and deuterated coronene, Fig. 5a and Fig. 5c respectively). Protonation and deuteration further increases the number of transitions in this region (Fig. 5d and Fig. 5e respectively). Cationic, protonated and deuterated forms of coronene show faint features at 3050 cm^{-1} ($3.3 \text{ }\mu\text{m}$) unlike the neutral counterparts.

From the data presented in Table 1-3, it is deduced that the C – D in-plane and H – C – D oop modes overlap the regions corresponding to C – H oop and C – H in-plane modes, respectively. The C – D stretching modes do not overlap with any other

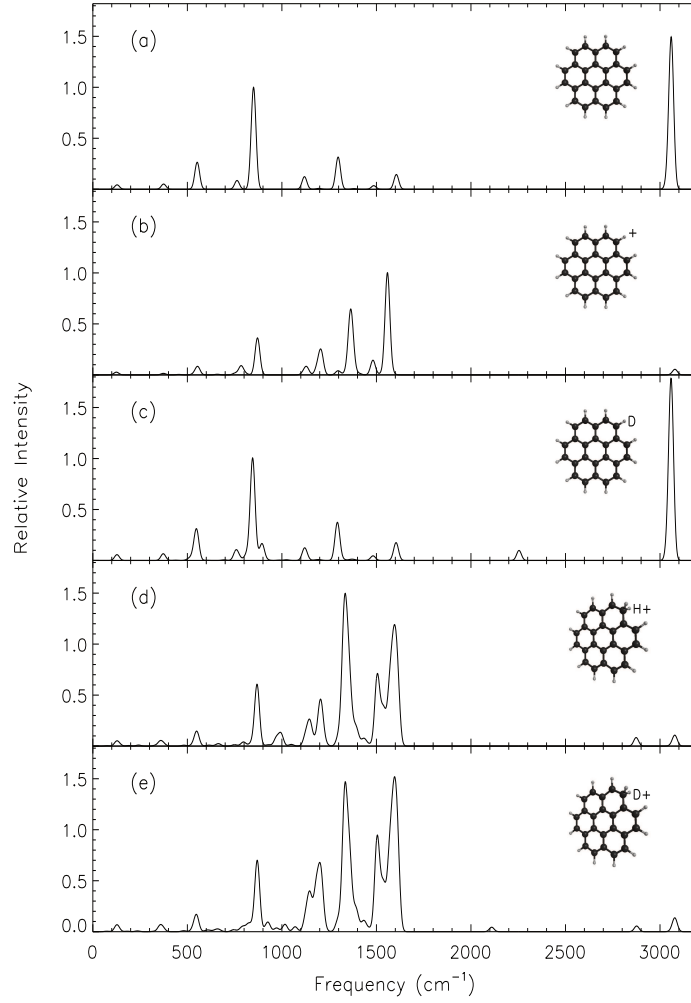


Figure 5. Theoretical spectra of (a) Neutral coronene, (b) Coronene cation, (c) Deuterated coronene, (d) Protonated coronene and (e) Deuterated coronene

Table 3. Theoretical spectral data for Deuterated coronene

DPAH ⁺	Frequency (cm ⁻¹)	Wavelength (μ m)	Relative Intensity	Mode
Deuterated Coronene	823	12.15	0.07	C – D in plane + C – H oop
	863	11.59	0.15	C – D in plane + C – H oop
	871	11.48	0.6	C – D in plane + C – H oop
	1181	8.47	0.34	H – C – D oop + C – H in plane

mode and are identified easily. For all three molecules along with their isomers (discussed above), C – D in plane modes are found to be distributed in the range $\sim 700 - 870$ cm⁻¹ ($14 - 11$ μ m) with a range of intensities. The H – C – D oop modes appear in the narrow range $\sim 1120 - 1212$ cm⁻¹ ($8.9 - 8.3$ μ m). A less intense feature is seen at ~ 2105 cm⁻¹ (4.75 μ m) which arises due to the C – D stretching mode of DPAH⁺. Symmetrical deuterated

pyrene (C_{2v}) shows a greater number of transitions compared to deuterated perylene (C_s) and deuterated coronene (C_s).

Peeters et al. (2004) reported the detection of PAD features at 4.4 μ m and 4.65 μ m towards the Orion Nebula and M17 with the use of *SWS* on board *ISO*. Onaka et al. (2014) using *AKARI* observed an overlapping region but did not confirm the detection and suggested the presence of similar bands with much weaker in-

tensity. Moreover, Onaka et al. (2014) did not look at the excess around $4.75\ \mu\text{m}$ region. The observations of Peeters et al. (2004) covered a larger area of Orion and M17 compared to the observations of Onaka et al. (2014) owing to the large aperture of the SWS ($20'' \times 14''$) on-board the *ISO* compared to the *IRC* ($Ns - 0'.8 \times 5''$ and $Nh - 1' \times 3''$) on *AKARI*. The detections of the 4.4 and $4.65\ \mu\text{m}$ bands reported by Peeters et al. (2004) have large uncertainties and are at a level of $4.4\ \sigma$ and $1.9\ \sigma$ respectively in M17 and Orion. Stretching of the C – D aromatic and C – D aliphatic bonds in PADs produce bands close to $4.4\ \mu\text{m}$ and $4.65\ \mu\text{m}$ respectively. These bands are analogous to the 3.3 and $3.5\ \mu\text{m}$ bands which arise due to aromatic and aliphatic C – H stretching respectively. From their observations, Peeters et al. (2004) calculated the D/H ratio (0.17 ± 0.03 towards the Orion bar and 0.36 ± 0.08 towards M17) by taking the ratio of the sum of intensities for bands in the $4 - 5\ \mu\text{m}$ (C – D stretching) region to the analogous sum near $3.3\ \mu\text{m}$ band (C – H stretching). Onaka et al. (2014) proposed a significantly smaller D/H ratio of $0.02 - 0.03$.

5 THEORETICAL SPECTRA FOR DEUTERATED-DEUTERONATED CORONENE AND DEUTERONATED CIRCUMCORONENE

Fig. 6 shows the calculated spectrum of deuterated-deuteronated coronene (DcorD^+). In DcorD^+ , a deuterium atom replaces a hydrogen atom to form a C – D bond and a deuteron (D^+) is added to a C – H site of the neutral coronene ($\text{C}_{24}\text{H}_{12}$). The resulting DcorD^+ molecule thus carries two types of C – D bond, ‘aromatic’ at the addition site of D and aliphatic at the addition site of D^+ . The spectrum is very similar to that of deuterated coronene except for a variation in intensity in the $\sim 1318 - 1570\ \text{cm}^{-1}$ ($7.6 - 6.4\ \mu\text{m}$) region. There are weak bands at $2110\ \text{cm}^{-1}$ ($4.7\ \mu\text{m}$), $2261\ \text{cm}^{-1}$ ($4.4\ \mu\text{m}$) and $2876\ \text{cm}^{-1}$ ($3.5\ \mu\text{m}$) with relative intensities of 0.07, 0.01 and 0.08 respectively. Absolute intensities for these particular bands are $7.4811\ \text{km/mole}$, $1.2101\ \text{km/mole}$ and $9.3345\ \text{km/mole}$ respectively. The $4.4\ \mu\text{m}$ feature is barely visible in the spectrum. As discussed earlier, these transitions are characteristic of aliphatic C – D stretching, aromatic C – D stretching and aliphatic C – H stretching, respectively.

DFT calculations were also performed on a large-sized DPAH^+ , i.e. deuterated circumcoronene ($\text{DC}_{54}\text{H}_{18}^+$), to investigate the effect of PAH size on the intensity and position of the C – D stretching mode. As shown in Fig. 7, the C – D stretching mode at $\sim 2127\ \text{cm}^{-1}$ ($4.7\ \mu\text{m}$) for deuterated circumcoronene is too weak to be visible. The absolute and relative intensity for this mode are $1.3165\ \text{km/mole}$ and 0.003, respectively.

With increase in size of DPAH^+ , the absolute and relative intensities of the C – D stretching transitions and the $[\text{D}/\text{H}]_{\text{num}}$ ratio (number of D atoms/number of H atoms) decrease (Table 4). DcorD^+ has two D atoms unlike other DPAH^+ s considered and hence has a higher $[\text{D}/\text{H}]_{\text{num}}$ ratio of 0.18. Another point to note is that as the size of the DPAH^+ increases, the band corresponding to the aliphatic C – D stretching mode shifts towards shorter wavelengths and closer to the observed astronomical band position of $4.65\ \mu\text{m}$. The absolute intensity, relative intensity and the position of the aliphatic C – D stretching mode for deuterated pyrene, deuterated perylene, deuterated coronene, DcorD^+ and deuterated circumcoronene are compared in Table 4. $[\text{D}/\text{H}]_{\text{int}}$ ratio has been determined by taking the ratio of the intensities of the C – D stretch bands to the intensities of the C – H stretch bands as obtained from the cal-

culations. There is no correlation present between $[\text{D}/\text{H}]_{\text{int}}$ and $[\text{D}/\text{H}]_{\text{num}}$. Having the same $[\text{D}/\text{H}]_{\text{num}}$ ratio, deuterated perylene and deuterated coronene give $[\text{D}/\text{H}]_{\text{int}}$ ratios of nearly same magnitude. DcorD^+ having two D atoms shows a higher $[\text{D}/\text{H}]_{\text{int}}$ ratio of 0.26 compared to that of deuterated coronene (one D atom). An exception is deuterated circumcoronene for which the $[\text{D}/\text{H}]_{\text{int}}$ ratio is lower by an order of magnitude compared to $[\text{D}/\text{H}]_{\text{num}}$ ratio. $[\text{D}/\text{H}]_{\text{int}}$ ratio is dependent on the size of PAHs and percentage of deuteration. Hence, for a comparative analysis, we compute $[\text{D}/\text{H}]_{\text{sc}}$ which is $[\text{D}/\text{H}]_{\text{int}}$ per $[\text{D}/\text{H}]_{\text{num}}$ (Table 4). $[\text{D}/\text{H}]_{\text{sc}}$ is found to be decreasing with increase in size of the molecule.

6 DPAH⁺ MOLECULES AS CARRIERS OF UIR EMISSION FEATURES

From the discussion above, it is established that deuterium containing PAHs (PADs and DPAH^+ s) show features in the $4 - 5\ \mu\text{m}$ region. This is the same region where spectral contribution of deuterated PAHs have been discussed by Peeters et al. (2004) and more recently by Onaka et al. (2014). This region is featureless for PAHs without deuterium. The position of the C – D stretch (aromatic and aliphatic) in PADs and DPAH^+ s are close to the 4.4 and $4.65\ \mu\text{m}$ emission bands observed towards the Orion Nebula and M17 (Peeters et al. 2004). The $4.65\ \mu\text{m}$ band in DPAH^+ is accompanied by a transition at $3.5\ \mu\text{m}$ corresponding to the aliphatic C – H stretch. Thus, a condition for DPAH^+ s to be present in the ISM is that the bands at $4.65\ \mu\text{m}$ and $3.5\ \mu\text{m}$ should be observed together in the emission spectra of an astronomical source. In the emission spectra of Orion nebula and M17 (Peeters et al. 2004), these two bands have indeed been detected which is an indicative of the presence of DPAH^+ molecules. In the M17 spectra, Peeters et al. (2004) have reported the detection of only the $4.65\ \mu\text{m}$ band at $4.4\ \sigma$ level (the detection of the $4.4\ \mu\text{m}$ feature towards Orion is with much higher uncertainty). This is a tentative yet strong evidence in support of the presence of deuterated-PAHs and / or aliphatic deuterated-PAHs. The presence of an aliphatic C – D bond results in a band at $4.65\ \mu\text{m}$ rather than the $4.4\ \mu\text{m}$ feature which arises due to an aromatic C – D stretch vibration. The aliphatic bond also results in features near $3.5\ \mu\text{m}$ that may indicate the presence of aliphatic C – H bonds in neutral and ionized (protonated) PAHs.

In this work we have focused on comparing the band position of DPAH^+ molecules with observations rather than correlating the intensity of the bands. Therefore, we have not taken into account the effect of excitation of the bands and their intensity. However, for a direct comparison with the observed spectra, the excitation mechanisms have to be considered. The C – D stretch bands being at lower wavenumbers are easily excited compared to the C – H stretch bands, thus, care has to be taken while comparing the theoretical and the observed D/H ratios. Onaka et al. (2014) calculated the emission intensity considering the effect of excitation based on a PAH emission model by Mori et al. (2012) and found that the smaller cross-section of the C – D stretch bands is compensated by its easier excitation compared to C – H stretch vibrations. They reported that excitation does not affect the result significantly but an overestimation of D/H ratio by tens of percent is present. We have computed $[\text{D}/\text{H}]_{\text{sc}}$ for DPAH^+ molecules, which is nothing but the ratio of C – D stretch and C – H stretch bands per $[\text{D}/\text{H}]_{\text{num}}$.

The observational $[\text{D}/\text{H}]$ values are estimated by assuming that the band strength per bond is constant for the C – H and

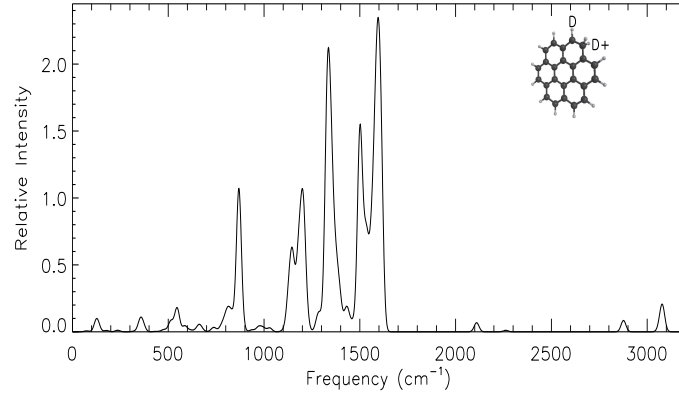


Figure 6. Theoretical spectrum of deuterated-deuteronated coronene (DcorD⁺)

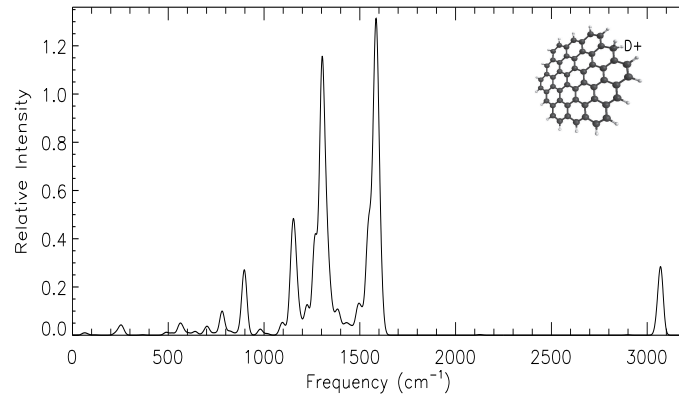


Figure 7. Theoretical spectrum of deuterated circumcoronene

Table 4. Intensities and positions of aliphatic C – D stretching mode in DPAH⁺s

DPAH ⁺	Frequency (cm ⁻¹)	Wavelength (μm)	Absolute Intensity (km/mole)	Relative Intensity	[D/H] _{num} ^a	[D/H] _{int} ^b	[D/H] _{sc} ^c
Deuteronated Pyrene	2092	4.78	18.1282	0.138	0.10	0.500	5.00
Deuteronated Perylene	2087	4.79	14.0726	0.063	0.08	0.271	3.39
Deuteronated Coronene	2110	4.74	7.3279	0.044	0.08	0.217	2.71
DcorD ⁺	2110	4.74	7.4811	0.068	0.18	0.258	1.43
Deuteronated Circumcoronene	2127	4.70	1.3165	0.003	0.06	0.008	0.13

^a [D/H]_{num} = no of D atoms/no of H atoms

^b [D/H]_{int} = intensity of C – D stretch/intensity of C – H stretch

^c [D/H]_{sc} = $\frac{[D/H]_{int}}{[D/H]_{num}}$

C – D bonds. This assumption may not hold for the C – D bond. These values are compared to the theoretically calculated $[D/H]_{sc}$ values of specific molecules. The $[D/H]_{sc}$ values for deuterated pyrene, deuterated perylene, deuterated coronene and $DcorD^+$ do not fall in the range of the D/H value given by observations (Peeters et al. 2004; Onaka et al. 2014). With increase in the size of $DPAH^+$ s, the $[D/H]_{sc}$ value tends to decrease. Observations reported by Peeters et al. (2004) suggest D/H values of 0.17 ± 0.03 in the Orion bar and 0.36 ± 0.08 in M17. However, Onaka et al. (2014) estimate a significantly smaller D/H value of 0.03 which is an order of magnitude smaller than the value proposed by Peeters et al. (2004); which points to the fact that if Ds are depleted onto PAHs, they might be accommodated in large PAHs (Onaka et al. 2014). Large PAHs have a tendency to be ionized in the ISM which may subsequently add a deuterium to form $DPAH^+$. Therefore, in such interstellar regions, the formation of $DPAH^+$ s may be preferred over PADs. The D/H ratios proposed by Peeters et al. (2004) and Onaka et al. (2014) may be used to estimate the size of PADs or $DPAH^+$ s in the ISM. From this work, deuterated circumcoronene shows a $[D/H]_{sc}$ value close to Peeters et al. (2004) observation. For the smaller deuterated PAHs, the $[D/H]_{sc}$ values are higher by about an order of magnitude. It is noted that $DPAH^+$ molecules of the size of circumcoronene (54 carbon atoms) and larger satisfy the D to H ratio as observed by Peeters et al. (2004) and Onaka et al. (2014). This points to the fact the $DPAH^+$ molecules if present may have 50 or more carbon atoms.

Following the observed band ratio as found by Onaka et al. (2014), the $DPAH^+$ molecules present in the ISM should be large. If this assumption is strictly followed, only large $DPAH^+$ molecules with low values of $[D/H]_{num}$ will exist in the ISM and these will not be able to account for the inferred depletion of D (Draine 2006). The expected D/H without depletion is around 20 parts per million (ppm) and the minimum observed ratio is about 7 ppm. If this difference is attributed solely to the depletion of D onto PAHs then the necessary concentration of D/H (value of $[D/H]_{num}$) in PAHs would be 0.3. This points to the fact that large PAHs that match the D/H value estimated from observed band ratios will have lower elemental D/H values and therefore, will not match the depletion model values of Draine (2006). This discrepancy warrants for an extensive observational programme for the search of $DPAH^+$ and PAD molecules in the ISM. Theoretical and experimental spectroscopic studies are further needed to complement the observations. A refined depletion model of D on PAHs may thus be obtained based on the results of observations and spectroscopic studies.

7 CONCLUSION

Interstellar PAHs may have significant deuterium content with a D/H ratio as high as 0.3 (Draine 2006). In this context, we have calculated the vibrational spectra of deuterated PAHs and have compared them with those of the corresponding neutral, cationic, deuterated and protonated forms. The theoretical spectral data provides strong evidences in support of $DPAH^+$ molecules to be part of the interstellar PAH family and these may be responsible for some of the observed IR features. In particular, the generally featureless region of $4 - 5 \mu m$ of pure PAHs may be dominated by features due to C – D bond vibrations in $DPAH^+$ s or deuterated PAHs. Stretching of the aliphatic C – D bond gives a distinct transition near $4.7 \mu m$. This warrants for a look at the excess around $4.7 \mu m$ region in astronomical sources.

Our calculations of deuterated circumcoronene yield a D/H ($[D/H]_{sc}$) value that is similar to ones obtained by Peeters et al. (2004). Large $DPAH^+$ s will have even small D/H values that might be in accordance with the proposed value of Onaka et al. (2014). A higher deuterium fraction has been observed in M17 (Peeters et al. 2004) with lower uncertainty which only shows the $4.65 \mu m$ band (the aliphatic deuterium bond) and not the $4.4 \mu m$ band (the aromatic deuterium bond). This clearly points to the dominance of deuterated-PAHs compared to deuterated-PAHs in such regions.

This study may also be used as input to deuterium depletion models and also for estimating the HD/H₂ ratio in interstellar gas. However for a more conclusive analysis, extensive observations followed by laboratory experiments are desired. Revisiting some of the ISO, AKARI and SPITZER data focusing on PAD and $DPAH^+$ systems may provide further insights. Upcoming James Webb Space Telescope may supplement this study by the addition of high quality data.

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